

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 743 172 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
04.08.1999 Bulletin 1999/31

(51) Int. Cl.⁶: B31F 1/12, D21H 17/72,
D21H 17/74

(21) Application number: 96303464.0

(22) Date of filing: 15.05.1996

(54) Novel creping adhesive formulations, method of creping and creped fibrous web

Neue adhesive Zusammensetzungen zum Kreppen, Verfahren zum Kreppen und gekrepptes fibröses Gewebe

Nouvelle formule adhésive de crêpage, méthode de crêpage et nappe fibreuse crêpée

(84) Designated Contracting States:
DE ES FR GB

(30) Priority: 18.05.1995 US 443941

(43) Date of publication of application:
20.11.1996 Bulletin 1996/47

(73) Proprietor:
FORT JAMES CORPORATION
Richmond, VA 23217 (US)

(72) Inventors:
• Luu, Phuong Van
Appleton, WI 54915 (US)

• Neculescu, Cristian M.
Neenah, WI 54956 (US)
• Mews, Dawn M.
Plover, WI 54467 (US)

(74) Representative:
Cropp, John Anthony David et al
MATHYS & SQUIRE
100 Grays Inn Road
London WC1X 8AL (GB)

(56) References cited:
EP-A- 0 479 554 EP-A- 0 541 232
EP-A- 0 606 889 US-A- 5 246 545
US-A- 5 374 334 US-A- 5 382 323

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 743 172 B1

Description

[0001] This invention relates to papermaking. More particularly, this invention is concerned with the manufacture of grades of paper that are suitable for use in paper toweling, napkins, facial tissue, and bathroom tissue by methods that include creping utilizing novel adhesives used as creping process aids.

BACKGROUND OF THE INVENTION

[0002] In the manufacture of tissue and towel products, a common step is the creping of the product. This creping is done to provide desired aesthetic and performance properties to the product. Many of the aesthetic properties of tissue and towel products rely more upon the perceptions of the consumer than on properties that can be measured quantitatively. Such things as softness, and perceived bulk are not easily quantified, but have significant impacts on consumer acceptance. Since many of the properties of tissue and towel products are controlled or are at least influenced by the creping process, it is of interest to develop methods for controlling the creping process. Although the creping process is not well understood, it is known that changes in the process can result in significant changes in the product properties. A need exists to provide a method for influencing the creping process by allowing the control of the adhesion of the tissue or towel substrate to the surface from which it is creped, most usually large cylindrical dryers known in the industry as Yankee dryers.

[0003] Paper is generally manufactured by suspending cellulosic fibers of appropriate length in an aqueous medium and then removing most of the water to form a web. The paper derives some of its structural integrity from the mechanical arrangement of the cellulosic fibers in the web, but most by far of the paper's strength is derived from hydrogen bonding which links the cellulosic fibers to one another. With paper intended for use as bathroom tissue, the degree of strength imparted by this interfiber bonding, while necessary to the utility of the product, results in a lack of perceived softness that is inimical to consumer acceptance. One common method of increasing the perceived softness of bathroom tissue is to crepe the paper. Creping is generally effected by fixing the cellulosic web to the surface of a dryer e.g. a drum dryer such as a Yankee drum thermal drying means with an adhesive/release agent combination and then scraping the web off of the surface by means of a creping blade. Creping, by breaking a significant number of interfiber bonds, increases the perceived softness of resulting bathroom tissue product.

[0004] In the past, common classes of thermosetting adhesive resins which have been used as creping adhesives have been represented by poly (aminoamide)-epichlorohydrin polymers (hereinafter referred to as PAE resins), such as those polymers sold under the tradenames Kymene, Rezsol, Cascamid, and Amreze. Each of these materials represent products sold respectively by the Hercules Chemical Company, the Houghton Company, the Borden Company, and Georgia-Pacific. Although these materials are now in commercial use, our novel adhesive formulations are environmentally friendly and have lower in-use cost.

[0005] This invention provides adhesion which is equal or better than the adhesion characteristics available through the use of PAE resins but having none of the attendant environmental problems associated with the halogen moiety. The halogen free, particularly chloride free, creping adhesives of this invention prevent or inhibit chloride or halogen induced corrosion of the dryer, e.g. Yankee drum, surface and, also, are friendly to the environment and have a lower in use cost.

[0006] Obtaining and maintaining adhesion of tissue and towel products to dryers is an important factor in determining crepe quality. Inadequate adhesion results in poor or non-existing creping, whereas excessive adhesion may result in poor sheet quality and operational difficulties. Traditionally, creping adhesives alone or in combination with release agents have been applied to the surface of the dryer in order to provide the appropriate adhesion to produce the desired crepe. Various types of creping adhesives have been used to adhere fibrous webs to dryer surfaces such as Yankee dryers. Some examples of prior art creping adhesives are disclosed in U.S.-A-4,886,579; 4,528,316 and 4,501,640.

[0007] U.S.-A-5,246,544 describes a creping adhesive that provides the ability to control coating mechanical properties and adhesion, and which can be more easily removed from dryer surfaces. The adhesive system described in said patent provides high adhesion of a fibrous web to dryer surface with low "friction". Having low friction means that the fibrous web can easily be removed from the dryer surface. Other references of interest include U.S.-A-5,232,553 and 4,684,439. All the prior art patents are of interest but do not disclose polymers having at least one primary or secondary amine group in the backbone such as chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine, polyaminoamide and etc., in combination with the dialdehydes or the zirconium crosslinking compounds having a valence of plus four such as ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate. These patents also do not relate to creping adhesives or the creping of tissue and towel from a Yankee dryer. U.S.-A-5,374,334 and 5,382,323 relate to adhesives reacted with the crosslinking agent prior to establishing contact with the dryer surface.

[0008] EP-A-0 479 554 discloses a method of creping a fibrous web which comprises providing to the interface of a

fibrous web and a support surface, preferably a drying surface such as provided by a Yankee dryer, a creping adhesive comprising a non-self-cross linkable material such as a polymer or oligomer having functional groups which are cross linkable by ionic cross-linking, and a cross linking agent which preferably comprises metal cations having a valency of at least three; e.g. zirconium with a valency of 4, and removing the fibrous web from the support surface by creping.

[0009] US-A-5 246 545 discloses a process for making soft tissue paper which includes providing a dry tissue web and then applying a sufficient amount of a chemical paper making additive from a thin film to the dry web. As creping adhesive polyvinyl alcohol is used. This document further discloses webs including a nitrogenous softener/debinder.

[0010] In our novel process the crosslinking agents are either charged to the dryer surface at the same time as the adhesive polymer or are mixed shortly prior to charging the polymer and crosslinking agent mixture to the Yankee surface without reacting the crosslinking agent with the polymer.

SUMMARY OF THE INVENTION

[0011] The present invention provides creping adhesives which are friendly to the environment giving off no chlorine compound pollutants, can be applied directly to the dryer, e.g. Yankee from aqueous solution and are substantially less costly than the presently available creping adhesives. The present invention provides an improved creping adhesive which provides the ability to readily control glass transition (T_g) and adhesion and which can be more easily removed from dryer surfaces.

[0012] An advantageous feature of the present invention is that the adhesion properties of specific types of polymers or copolymers (hereinafter referred to as base polymers) can be systematically changed by varying the amount of crosslinking that may occur when the base polymer is dried onto the surface of a Yankee dryer with the zirconium or dialdehyde crosslinking agents. Because crosslink density influences the mechanical properties (i.e., modulus, brittleness, T_g), this permits the adjustment of adhesion/release of the fibrous substrate onto the surface of the dryer. Base polymers having at least one primary or secondary amine groups in the backbone such as chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine, polyaminoamide and etc., crosslinked with dialdehydes or zirconium compounds having a valence of plus four produce an adhesive friendly to the environment and which is much less costly than the PAE resin available on the market as discussed in the background section. The invention also relates to a process for applying such base polymers without pre-crosslinking to achieve adhesion control on the paper machine through spray application. This invention also relates to creped fibrous webs, creped tissue and creped towel and a process for the manufacturing of these paper products utilizing the novel adhesives of this invention.

[0013] In accordance with one aspect of the present invention, there is provided a creping adhesive composition comprising an organic polymer having in the polymer backbone amine groups selected from primary and secondary amine groups and mixtures thereof and a crosslinking agent for crosslinking the polymer to itself and to the fibrous web, said agent being selected from zirconium compounds wherein the zirconium has a valency of plus four.

[0014] This invention also provides a method of forming a creped fibrous web using this adhesive composition and a creped fibrous web made using the composition.

[0015] In accordance with another aspect of the invention, there is provided a creped fibrous web made using, as the creping adhesive, a composition comprising an organic polymer having in the polymer backbone amine groups selected from primary and secondary amine groups and mixtures thereof and a crosslinking agent for crosslinking the polymer to itself and to the fibrous web, said agent being selected from dialdehydes, said web further including a nitrogenous softener/debinder.

[0016] In accordance with yet another aspect of the invention there is provided a method of creping a fibrous web which includes adhering it to a dryer surface with a creping adhesive composition and thereafter creping it from the surface characterised in that the creping adhesive composition comprises an organic polymer having in the polymer backbone amine groups selected from primary and secondary amine groups and mixtures thereof and a crosslinking agent for crosslinking the polymer to itself and to the fibrous web said agent being selected from dialdehydes, and the crosslinking agent and organic polymer are applied separately to the dryer surface whereby crosslinking takes place on the dryer surface. Alternatively, the crosslinking agent and the organic polymer are mixed together just prior to contact with the dryer surface whereby crosslinking substantially takes place on the dryer surface.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The present invention will now be described in greater detail with reference to preferred embodiments and with the aid of the accompanying drawings which illustrate the application of the invention in a papermaking process employing a Yankee dryer as illustrative of the drying means (although it should be understood that the invention is also applicable to other drying means, e.g. through air dryers) and wherein:

Figure 1 illustrates a paper making process.

Figure 2 illustrates in detail the Yankee dryer employed in the scheme and the position from which the base polymer and the crosslinking agent, and if necessary, the softener can be sprayed on the Yankee or the web.

Figure 3 illustrates the effect of glyoxal crosslinking agent on polyvinyl alcohol (PVOH) Yankee adhesion, as measured by peel force, for different molecular weight and hydrolysis degrees.

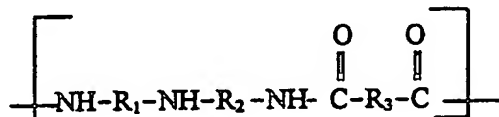
Figure 4 illustrates the effect of glyoxal crosslinking agent on polyvinyl alcohol-vinyl amine copolymer adhesion and blend with unfunctionalized polyvinyl-alcohol, as measured by peel force with and without softener.

Figure 5 illustrates the GMT (grams/76.2 mm) (grams/3 inches) versus the glyoxal level incorporated into the base polymer such as polyvinyl alcohol-vinyl amine copolymer, and blend with unfunctionalized polyvinyl alcohol, with and without softener.

DETAILED DESCRIPTION OF THE INVENTION

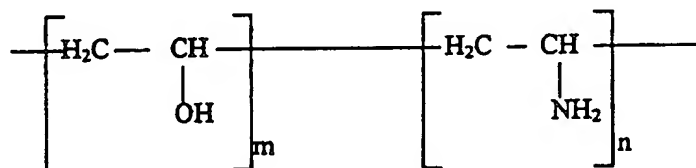
[0018] In accordance with the present invention, a method is provided for producing a highly absorbent, cellulosic sheet having a high level of perceived softness that comprises continuously a) preparing an aqueous dispersion of cellulosic papermaking fibers, b) forming a web of said cellulosic papermaking fibers, c) adhering the web to a dryer surface such as a Yankee dryer with base polymers wherein suitably the base polymer can have both primary and secondary amine groups or a mixture of primary and secondary amine groups. Representative base polymers include polyvinyl alcoholvinyl amine copolymers, chitosan, polyvinylamine and polyaminoamide. The base polymers are crosslinked with materials such as dialdehydes or zirconium compounds having a valence of plus four. The base polymers having at least one primary or secondary amine group or a mixture of primary and secondary amine groups are prepared according to the methods disclosed in the following U.S. Patents: US-A-5,155,167; 5,194,492; 5,300,566; 4,574,150; 4,286,087; 4,165,433; 3,892,731; 3,879,377; 2,926,154 and 2,926,116. The cellulosic sheet was creped from the Yankee dryer by a creping blade thus providing a higher degree of perceived softness. Suitable paper products obtained utilizing the novel adhesives include single and multi ply tissue and towel.

[0019] Useful polyaminoamides have the following repeating unit structure:

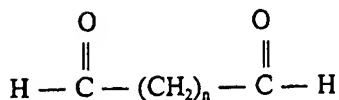


wherein R_1 and R_2 have two to eight aliphatic carbon atoms and R_3 has two to six carbon atoms.

[0020] The preferred polyvinyl alcohol ad polyvinylamine copolymer has the following structure:



where m and n have values of about 1 to 99 and about 99 to 1. Advantageously the values of m and n are about 1 to 99 and about 2 to 20. The polyvinyl alcohol-vinyl amine copolymer can have impurities which comprise the unhydrolyzed starting product. The structure of an impure product is disclosed in U.S.-A-5,300,566 and 5,194,492. The crosslinking agent sprayed with the polyvinyl alcohol-vinyl amine copolymer as shown in Figure 2 at position 51 is a dialdehyde such as glyoxal or glutaldehyde and etc., or a zirconium compound having a valence of plus four such as ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate. The zirconium crosslinking agents and polyvinyl alcohol-vinyl amine base polymer are sprayed separately at the same time on the Yankee surface. The dialdehydes are mixed with the base polymer just prior to spraying so that the dialdehyde and base polymer have no practical chance to react prior to reaching the heated Yankee surface. The crosslinking agent and base polymer are reacted directly on the Yankee surface. Spraying the adhesive on the Yankee is the best mode of application of the adhesives. Suitable dialdehydes are glyoxal, malonic, succinic, and glutaric dialdehyde. Suitably these aldehydes can be represented by the following structural formula:



wherein n is an integer having a value of 0 to 3. The preferred aldehydes are glyoxal and glutaraldehyde. In some applications for the manufacture of tissue and towel, suitable softeners are utilized. The softeners are sprayed on the web as shown in Figure 2 from position 52 or 53.

[0021] The novel adhesives are environmentally friendly and are very capable of ready application to the Yankee surface from aqueous solution. Additionally the adhesives are substantially less expensive than present PAE resin products.

[0022] For the sake of simplicity, the invention will be described immediately herein below in the context of a conventional dry crepe wet-forming process. A schematic drawing depicting a process configuration is set forth in Figure 1.

[0023] The paper products, such as tissue and towel, of the present invention may be manufactured on any paper-making machine of conventional forming configurations such as fourdrinier, twin-wire, suction pressure roll or crescent forming configurations. The forming mode is advantageously water or foam. Figure 1 illustrates an embodiment of the present invention wherein a machine chest 50 is used for preparing furnishes that may mutually be treated with chemicals having different functionality depending on the character of the various fibers, particularly fiber length and coarseness. The furnishes are transported through conduits 40 and 41 where the furnishes are delivered to the headbox of a crescent forming machine 10. This Figure 1 includes a web-forming end or wet end with a liquid permeable foraminous support member 11 which may be of any conventional configuration. Foraminous support member 11 may be constructed of any of several known materials including photo polymer fabric, felt, fabric or a synthetic filament woven mesh base with a very fine synthetic fiber batt attached to the mesh base. The foraminous support member 11 is supported in a conventional manner on rolls, including press roll 15 and couch roll or pressing roll 16.

[0024] Forming fabric 12 is supported on rolls 18 and 19 which are positioned relative to the press roll 15 for pressing the press wire 12 to converge on the foraminous support member 11 at the cylindrical press roll 15 at an acute angle relative to the foraminous support member 11. The foraminous support member 11 and the wire 12 move in the same direction and at the same speed which is the same direction of rotation of the pressure roll 15. The pressing wire 12 and the foraminous support member 11 converge at an upper surface of the forming roll 15 to form a wedge-shaped space or nip into which two jets of water or foamed-liquid fiber dispersion is pressed between the pressing wire 12 and the foraminous support member 11 to force fluid through the wire 12 into a saveall 22 where it is collected for reuse in the process.

[0025] A wet nascent web W formed in the process is carried by the foraminous support member 11 to the pressing roll 16 where the wet nascent web W is transferred to the drum 26 of a Yankee dryer. Fluid is pressed from the wet web W by pressing roll 16 as the web is transferred to the drum 26 of the Yankee dryer where it is dried and creped by means of a creping blade 27. The finished web is collected on a take-up roll 28.

[0026] A pit 44 is provided for collecting water squeezed from the nascent web W by the press roll 16 and the Uhle box 29. The water collected in the pit 44 may be collected into a flow line 45 for separate processing to remove surfactant and fibers from the water and to permit recycling of the water back to the papermaking machine 10. The liquid, suitably foamed liquid, is collected from the furnish in the saveall 22 and is returned through line 24 to a recycle process generally indicated by box 50.

[0027] Dewatering of the wet web is provided prior to the thermal drying operation, typically by employing a nonthermal dewatering means. The nonthermal dewatering step is usually accomplished by various means for imparting mechanical compaction to the web, such as vacuum boxes, slot boxes, coacting press rolls, or combinations thereof. For purposes of illustration of the method of this invention, the wet web may be dewatered by subjecting same to a series of vacuum boxes and/or slot boxes. Thereafter, the web may be further dewatered by subjecting same to the compressive forces exerted by nonthermal dewatering means such as, for example, utilizing roll 15, followed by a pressure roll 16 coacting with a thermal drying means. The wet web is carried by the foraminous conveying means 11, 12 through the nonthermal dewatering means, and is dewatered to a fiber consistency of at least about 5% up to about 50%, preferably at least 15% up to about 45%, and more preferably to a fiber consistency of approximately 40%.

[0028] The dewatered web is applied to the surface of thermal drying means, preferably a thermal drying cylinder such as a Yankee drying cylinder 26, employing the dialdehyde or zirconium crosslinking agent having a valence of plus four with the polyvinyl alcohol-vinyl amine copolymer. Under the definition of "Yankee" is included all large cast iron drying cylinders some of which may be ceramic coated on which towel, tissue, wadding, and machine-glazed papers are among the grades produced. Diameters typically range from 3.05-6.10 m (10-20 feet) and widths can approach 7.62 m (300 inches) A typical diameter for a Yankee drying drum is 3.66 m (12 feet.) Speeds in excess of 1829m/min (6000

ft/min) at weights greater than 172,365 kg (380,000 pounds) are not uncommon. Dryers typically incorporate a center shaft and are supported on journals by two large antifriction bearings. Steam, up to 1.1 MPa gauge (160 psig) (Code limitation for cast-iron unfired pressure vessels) is supplied through the front-side journal and exhausted, along with condensate, through the back-side journal. A typical steam pressure is 0.86 MPa gauge (125 psig). Pressure rolls 16, one or two usually loaded between 3571 and 8929 kg/m (200 and 500 pounds/linear inch), are employed to press the sheet uniformly against the shell face. The sheet is removed from the dryer several quadrants away, having been imparted with properties characteristic of the desired paper product.

[0029] Adhesion of the dewatered web to the cylinder surface is facilitated by the mechanical compressive action exerted thereon, generally using one or more press rolls 16 that form a nip in combination with thermal drying means 26. This brings the web into more uniform contact with the thermal drying surface.

[0030] Since we prefer to use high adhesion creping to quantify the degree of adhesion, we define adhesion as the force in grams required to peel a 0.304 m (12 inch) wide sheet off the creping cylinder at a 90 degree angle with the creping blade in the off-load position. We have found that using the creping adhesive of this invention, it is possible to control adhesion such that the junction between the sheet and Yankee (26) exhibits relatively high adhesion compared to conventional adhesives which include PAE resins. High adhesion level is preserved when our crosslinkable adhesive formulations are used as the creping process aids in the presence of softener and debonder. Specifically, when softener is used in the range of 0.05 to 0.5 weight percent one (1) to about ten (10) pounds per ton, adhesion is good as defined by the peel force of about 0.98 g/mm to about 2.95 g/mm (300 to about 900 grams per 12 inches), when using a paper-making machine having a speed of less than 45.7 m/minute (one hundred fifty feet per minute (150 ft./minute)). Generally, when softener is added, adhesion is decreased. Unlike conventional adhesives of the PAE type and the like, utilization of our crosslinkable adhesive formulation in conjunction with softener, allows one to minimize the difference between air and Yankee side friction of the creped product while preserving overall low friction, all of which promote high quality crepe structure required for good tissue and towel softness.

[0031] Alternatively adhesion can be indirectly measured as sheet tension with the creping blade in on-load position. Sheet tension should be in the range of 1.97 to 4.92 g/mm (600 - 1,500 grams per 12 inches). The sheet tension is measured by the transducer idler roll positioned prior to take-up roll 28. If paper machine speed, basis weight, furnish refining and other operational parameters are kept constant, then sheet tension is a function of adhesion only.

[0032] Figure 2 illustrates the drying and creping of the cellulosic web to produce tissue and towel. According to our process, both one ply and multi-ply towel and tissue are produced. According to the process of the invention, the novel adhesives each comprising base polymer and crosslinking agent are sprayed directly on the Yankee (26) at position 51. In the event it is desired to use softeners, these are sprayed on the air side of the web from position 52 or 53 as shown in Figure 2. When using the zirconium crosslinking agent then both the base polymer and the crosslinking agent are sprayed separately but almost simultaneously on the heated Yankee surface.

[0033] The various components of the adhesive formulation, may all be dissolved, dispersed, suspended, or emulsified in a liquid carrying fluid. It should be noted that the crosslinking agents in our process are either sprayed directly on the Yankee surface with the base polymer or in case of the dialdehydes are mixed with the base polymer just prior to spraying. This liquid will generally be a non-toxic solvent such as water. The liquid component is usually present in an amount of 90 to 99% by weight of the total weight of the creping adhesive. The pH of the adhesive when it is applied to the desired surface in the papermaking operation will normally be about 7.5 to 11. The solvent preferably consists essentially or completely of water. If other types of solvents are added, they are generally added in small amounts.

[0034] Referring to the drawing in Figure 2, this represents one of a number of possible configurations used in processing tissue and towel products. In this particular arrangement, the transfer and impression fabric carries the formed, dewatered web W around turning roll 15 to the nip between press roll 16 and Yankee dryer 26. The fabric, web and dryer move in the directions indicated by the arrows. The entry of the web to the dryer is well around the roll from creping blade 27 which, as schematically indicated, crepes the traveling web from the dryer as indicated at 27. The creped web W exiting from the dryer is wound into a soft creped tissue, or towel at roll 28. To adhere the nascent web W to the surface of the dryer, a spray 51 of adhesive is applied to the surface ahead of the nip between the press roll 16 and Yankee 26. Alternately, the spray may be applied to the traveling web W directly as shown at 53. Suitable apparatus for use with the present invention are disclosed in U.S.-A-4,304,625 and 4,064,213.

[0035] This illustration does not incorporate all the possible configurations used in presenting a nascent web to a Yankee dryer. It is used only to describe how the adhesives of the present invention can be used to promote adhesion and thereby influence the crepe of the product. The present invention can be used with all other known processes that rely upon creping the web from a dryer surface. In the same manner, the method of application of the adhesive to the surface of the dryer or the web is not restricted to spray applications, although these are generally the simplest method for adhesive application.

[0036] The present invention is useful for the preparation of fibrous webs which are creped to increase the thickness and bulk of the web and to provide texture to the web. The invention is particularly useful in the preparation of final products such as facial tissue, toilet tissue, paper towels, and the like. The fibrous web can be formed from various types of

wood pulp based fibers which are used to make the above products such as hardwood kraft fibers, softwood kraft fibers, hardwood sulfite fibers, softwood sulfite fibers, high yield fibers such as chemo-thermo-mechanical pulps (CTMP), thermomechanical pulps (TMP) or refiner mechanical pulps (RMP). Furnishes used may also contain or be totally comprised of recycled fibers (i.e., secondary fibers). The fibrous web, prior to application to the Yankee dryer, usually has a water content of 40 to 80 wt. %, more preferably 50 to 70 wt. %. At the creping stage, the fibrous web usually has a water content of less than 7 wt. %, preferably less than 5 wt. %. The final product, after creping and drying, has a basis weight of 11.39 to 48.8 g/m² (7 to 30 pounds) per ream.

[0037] The non-self-crosslinkable base polymer of the present invention called the base polymer, has at least one primary or secondary amine groups in the backbone such as chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine, polyaminoamide and etc., or combinations thereof and the crosslinking agents are dialdehydes or zirconium compounds having a valence of plus four. Suitable dialdehydes include glyoxal, malonic dialdehyde, succinic dialdehyde and glutaraldehyde. Suitable zirconium crosslinking agents include ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.

[0038] The non-self-crosslinkable base polymer should be present in the creping adhesive in an amount sufficient to provide the desired results in the creping operation. If it is intended to spray the creping adhesive onto the surface of the Yankee dryer, the creping adhesive should have a viscosity low enough to be easily sprayed yet high enough to provide a sufficient amount of adhesion. When the creping adhesive is sprayed onto the surface of the Yankee dryer, it should have a total solids content of about 0.01 to 0.5, preferably 0.03 to 0.2% by weight based on the total weight of the fiber. The solids content is constituted primarily by the base polymer and the dialdehyde or zirconium crosslinking agent. The zirconium crosslinking agent having a valence of plus four is sprayed separately on the Yankee surface and only comes in contact with the base polymer on the heated Yankee surface, whereby the combined action of drying and heating effect crosslinking required for adhesion.

[0039] The crosslinking agent should be present on the Yankee surface in the creping adhesive formulation in an amount sufficient to provide changes in the mechanical properties of the base polymer once the solution has been evaporated and the polymer crosslinked. As the level of crosslinking increases, the mechanical properties change with the crosslink density. Increased crosslinking generally will increase the T_g, increase the brittleness, hardness, and provide different responses to mechanical stresses than uncrosslinked polymers. Obtaining the appropriate crosslink density will depend not only on the relative concentration of added crosslinking agent but also on the molecular weight of the polymer. In general, as the molecular weight of the starting polymer increases, the amount of crosslinking agent necessary to provide particular levels of final properties (i.e., T_g, brittleness, etc.) decreases. A discussion concerning the relationship between T_g and crosslinking of polymers is contained in the article by Stutz et al., *Journal of Polymer Science*, 28, 1483-1498 (1990).

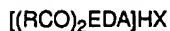
[0040] In our process the ratio of the base polymer to the crosslinking agent can be varied widely. The function of the crosslinking agent is to control adhesion. The weight ratio of the crosslinking agent to base polymer may go up to 4:1. The preferred ratio is about 0.05:1 to about 2:1. The base polymer can be a homopolymer or a copolymer. It should be noted that in our process all the crosslinking was activated on the heated Yankee surface.

[0041] While the base polymer and crosslinking agent are the major "active" ingredients of the present invention, other materials can be incorporated with beneficial results. Materials can be added to modify the mechanical properties of the crosslinked base polymers. Some of these materials may actually be incorporated into the crosslinked polymer. Examples would include glycols (ethylene glycol, propylene glycol, etc.), polyethylene glycols, and other polyols (simple sugars and oligosaccharides). Other components can be added to modify interfacial phenomena such as surface tension or wetting of the adhesive solution. Nonionic surfactants such as the octyl phenoxy based Triton (Rohm & Haas, Inc.) surfactants or the Pluronic or Tetronic (BASF Corp.) surfactants can be incorporated in the present invention to improve surface spreading or wetting capabilities. Mineral oils or other low molecular weight hydrocarbon oils or waxes can be included to modify interfacial phenomena and thereby control adhesion.

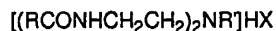
[0042] The non-self-crosslinking base polymer, polymer modifiers, surfactants, and anti-corrosion additives, will all be dissolved, dispersed, suspended, or emulsified in a liquid carrying fluid. This liquid will usually be a non-toxic solvent such as water. In our novel process the zirconium crosslinking agents such as ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate crosslinking agents were sprayed directly on the Yankee or alternately the dialdehyde was added to the adhesive formulation just prior to spraying on the Yankee surface to avoid reaction with the base polymer and the crosslinking agent prior to reaching the heated Yankee surface.

[0043] Nitrogenous softeners/debonders can suitably be added in the paper manufacturing process. The softener may suitably be added with the furnish, but is preferably sprayed from position 53 as shown in Figure 2, or also sprayed to the sheet while the sheet is on the Yankee as shown in Figure 2 position 52.

[0044] Representative softeners have the following structure;

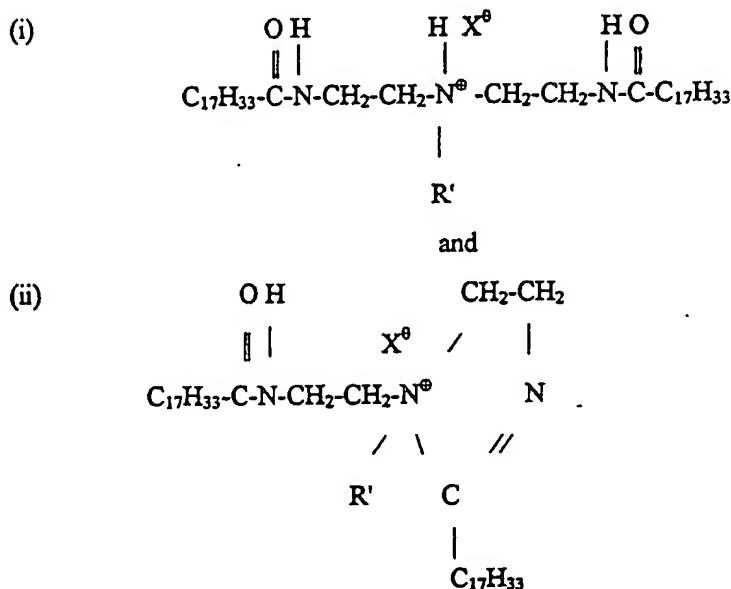


wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion or



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

[0045] The preferred softener is Quasoft® 202-JR and 209-JR made by Quaker Chemical Corporation which is a mixture of linear amine amides and imidazolines of the following structure:



wherein X is an anion.

[0046] As the nitrogenous cationic softener/debonder reacts with a paper product during formation, the softener/debonder either ionically attaches to cellulose and reduces the number of sites available for hydrogen bonding thereby decreasing the extent of fiber-to-fiber bonding or covalently attaches to the crosslinking agent to produce improved softness due to enhanced substantivity of softener to fiber.

[0047] The present invention may be used with a particular class of softener materials --amido amine salts derived from partially acid neutralized amines. Such materials are disclosed in U.S.-A-4,720,383; column 3, lines 40-41. Also relevant are the following articles: Evans, *Chemistry and Industry*, 5 July 1969, pp. 893-903; Egan, *J. Am. Oil Chemist's Soc.*, Vol. 55 (1978), pp. 118-121; and Trivedi et al., *J. Am. Oil Chemist's Soc.*, June 1981, pp. 754-756. As indicated therein, softeners are often available commercially only as complex mixtures rather than as single compounds. While this discussion will focus on the predominant species, it should be understood that commercially available mixtures would generally be used to practice the invention.

[0048] At this time, Quasoft® 202-JR and 209-JR is a preferred softener material which is derived by alkylating a condensation product of oleic acid and diethylenetriamine. Synthesis conditions using a deficiency of alkylating agent (e.g., diethyl sulfate) and only one alkylating step, followed by pH adjustment to protonate the non-ethylated species, result in a mixture consisting of cationic ethylated and cationic non-ethylated species. A minor proportion (e.g., about 10%) of the resulting amido amines cyclize to imidazoline compounds. Since these materials are not quaternary ammonium compounds, they are pH-sensitive. Therefore, in the practice of the present invention with this class of chemicals, the pH in the headbox should be approximately 6 to 8, more preferably 6 to 7 and most preferably 6.5 to 7.

[0049] The softener employed for treatment of the furnish is provided at a treatment level that is sufficient to impart a perceptible degree of softness to the paper product but less than an amount that would cause significant runnability and sheet strength problems in the final commercial product. The amount of softener employed, on a 100 % active basis, is preferably from about 0.05 g/Kg (0.1 pounds per ton) of fiber in the furnish up to about 5 g/Kg (10 pounds per ton) of fiber in the furnish, the more preferred amount is from about 1 g/Kg to about 2.5 g/Kg (2 to about 5 pounds per ton) of

fiber in the furnish.

[0050] Figures 3 through 5 demonstrate that dialdehydes are effective crosslinking agents when combined with a base polymer such as polyvinyl alcohol and polyvinyl alcohol-vinyl amine copolymer, and blend thereof.

[0051] Figures 4 and 5 illustrate that dialdehyde crosslinking increases adhesion in the presence of softener, as evidenced by higher adhesion values as measured by peel force and lower geometric mean tensile (GMT) parameters.

[0052] Esthetics and tactile considerations are extremely important for tissue products as they often come into intimate contact with the most delicate parts of the body in use. Consequently, demand is quite high for products with improved tactile qualities, particularly softness. However, as tissue products are frequently used to avoid contact with that which the consumer would greatly prefer not to touch, softness alone is not sufficient; strength is also required.

Merely providing a product with improved properties is not generally sufficient, the "on the shelf" appearance of the product must suggest both strength and softness while consumers must be able to sense improvements by hiding packaged product. Appearance is critical; bulk, weight, compressibility, firmness, texture and other qualities perceived as indicia of strength and softness are also required.

[0053] TAPPI 401OM-88 (Revised 1988) provides a procedure for the identification of the types of fibers present in a sample of paper or paperboard and estimation of their quality. Analysis of the amount of the softener/debonder chemicals retained on the tissue paper can be performed by any method accepted in the applicable art. For the most sensitive cases, we prefer to x-ray photoelectron spectroscopy ESCA to measure nitrogen levels. Normally, the background level is quite high and the variation between measurements quite high, so use of several replicates in a relatively modern ESCA system such as the Perkin Elmer Corporation's model 5600 is required to obtain more precise measurements. The level of cationic nitrogenous softener/debonder such as Quasoft® 202-JR can alternatively be determined by solvent extraction of the Quasoft® 202-JR by an organic solvent followed by liquid chromatography determination of the softener/debonder.

[0054] Tensile Strength of tissue produced in accordance with the present invention is measured in the machine direction and cross-machine direction on an Instron tensile tester with the gauge length set to 0.10m (4 inches). The area of tissue tested is assumed to be 0.08m (3 inches) wide by 0.10m (4 inches) long. A 9.07 kg (20 pound) load cell with heavyweight grips applied to the total width of the sample is employed. The maximum load is recorded for each direction. The results are reported in units of "grams per 76.2 mm (3-inch)"; a more complete rendering of the units would be "grams per 76.2 mm (3-inch) by 101.6 mm (4-inch) strip". 1g per 3-inch is 0.013g/mm

[0055] Softness is a quality that does not lend itself to easy quantification. J.D. Bates, in "Softness Index: Fact or Mirage?", TAPPI, Vol. 48 (1965), No. 4, pp. 63A-64A, indicates that the two most important readily quantifiable properties for predicting perceived softness are (a) roughness and (b) what may be referred to as stiffness modulus. Tissue and toweling produced according to the present invention have a more pleasing texture as measured by reduced values of either or both roughness or stiffness modulus (relative to control samples). Surface roughness can be evaluated by measuring geometric mean deviation in the coefficient of friction using a Kawabata KES-SE Friction Tester equipped with a fingerprint-type sensing unit using the low sensitivity range. A 25 g stylus weight is used, and the instrument readout is divided by 20 to obtain the mean deviation in the coefficient of friction. The geometric mean deviation in the coefficient of friction (GMMD) is then the square root of the product of the deviation in the machine direction and the cross-machine direction, thereafter is referred to as friction. The stiffness modulus is determined by the procedure for measuring tensile strength described above, except that a sample width of 25.4 mm (1 inch) is used and the modulus recorded is the geometric mean of the ratio of 50 grams load over percent strain obtained from the load-strain curve.

[0056] The STFI values set forth in tables 1, 6, 7 and 8 are obtained by the method disclosed in the publication of the proceedings at the *Tissue Making Conference*, October 5-6, 1989 in Karlstad, Sweden entitled Characterization of Crepe Structure by Image Analysis, Magnus Falk, STFI, Sweden, pp. 39-50. In our method, the tissue is placed under a stereo microscope with the Yankee side up and illuminated in the MD with oblique illumination roughly 10 degrees out of plane. Images (9) are collected at a magnification of 16X at 512x512x256 resolution and corrected for the nonuniformity in illumination. The images are segmented (transformed from greylevel to binary) such that 50% of the area is shadow. Nine equally spaced scans are conducted on each image and the shadow lengths determined and saved in a data base. The data are fitted interactively to an Erlang distribution to determine the best fit STFI length is related to crepe coarseness - i.e. a lower STFI number corresponds to a finer crepe structure which in turn contributes to higher perceived softness.

Example 1

[0057] This example illustrates the general papermaking process utilizing our adhesive formulations and optional softeners. Further data are set forth in Tables 1 and 2.

[0058] A furnish of 50% Northern hardwood kraft and 50% Northern softwood kraft was prepared. The papermaking machine was an inclined wire former with a Yankee dryer speed of 0.5 m/sec (100 ft. per minute). 91g (Two tenths of a pound) of base polymer with specified crosslinking agent amount per 1000 kg (ton) of furnish was sprayed directly on

the Yankee; the amount of softener sprayed on the Yankee side of the sheet is set forth in Table 1. The creping angle was maintained constant at 72°C. The bevel was 8°. The Yankee temperature was 101°C. The adhesive formulations were sprayed from position 51, as shown in Figure 2, directly on the Yankee, while the softeners, if used, were sprayed from position 52, as shown in Figure 2, which is the air side of the sheet on the Yankee.

Table 1
Adhesion and Sheet Physical Properties for Creping Adhesive Formulations

Creping System Formulation	Peel Force (g/12") (2)	Side Dev	Sheet Tension (g/12") (2)	Side Dev	MD Tensile (g/3") (3)	CD Tensile (g/3") (3)	GM Tensile (g/3") (3)	STIFFNESS (G/% STR-1M)	Friction	STFI Length (μm)
Houghlon (PAE)	735	46	1101	11	2216	969	1463	44.22	0.29	176
Houghlon 8290 (PAE) + 1 lb. (1) vinyl amine	547	9	740	3	2470	1103	1631	43.43	0.26	143
Softener per ton of furnish	818	50	1220	33	2513	1061	1633	53.66	0.28	174
A1 (6 mol % vinyl amine)										
A1 + 50 PHR glyoxal	786	29	1287	1	2223	939	1443	52.83	0.26	167
A1/Airvol 107 (4 mol % VA)	727	15	1149	2	2346	1160	1650	46.97	0.25	171
A1/Airvol 107 (4 mol % VA) + 50 PHR glyoxal	834	18	1179	2	2264	918	1441	44.77	0.27	166
A1/Airvol 107 (2 mol % VA)	618	34	1106	16	2440	1152	1676	50.42	0.28	177
A1/Airvol 107 (2 mol % VA) + 25 PHR glyoxal	616	20	1200	0	2553	1245	1783	—	—	179
A1 + 1 lb. softener per ton of furnish	480	93	765	90	2940	1465	2073	61.87	0.26	148
A1 + 1 lb. softener per ton of furnish + 50 PHR glyoxal	674	8	991	5	2376	1263	1804	62.12	0.29	140
A1 + 3 lb. softener per ton of furnish	236	17	337	12	2676	1019	1709	46.44	0.28	168
A1 + 3 lb. softener per ton of furnish + 50 PHR glyoxal	372	60	443	103	2427	978	1340	42.53	0.31	168

(1) Base polymer add on = 0.2 lbs per ton of furnish.

(2) PHR glyoxal = grams glyoxal per 100 g base polymer

(3) A1 = Polyvinyl alcohol - 6 mol % vinyl amine copolymer. Intermediate mol % vinyl amine contents achieved by blending A1 with unfunctionalized PVOH (Airvol 107).

(4) Airvol 107 = PVOH adhesive 98.4 percent hydrolyzed and having a molecular weight of 40,000 g/mol.

* STFI values determined from publication at Tissue Making Conference, October 3-6, 1989 in Karlstad, Sweden. Characterization of Crepe Structure by Image Analysis, Magnus Falk, STFI, Sweden, pp. 39-50.

$$(1) \text{ 1 lb per ton} = 0.05 \% \text{ by wgt}$$

$$(2) \text{ g/12"} = 3.3 \text{ g/m}$$

$$(3) \text{ g/3"} = 13.1 \text{ g/m}$$

Example 2

[0059] Examples 2 and 3 illustrate the manufacturing method for one and two ply tissues. The adhesive and softener data are not provided in these examples but are set forth in the subsequent examples.

[0060] A furnish of 50% Southern hardwood kraft and 50% Southern softwood kraft was prepared. The papermaking machine was an inclined wire former with a Yankee dryer speed of 1852 feet per minute. The operating data for the papermaking process are set forth in Table 2. A high basis weight base sheet was prepared.

Table 2

ONE PLY TISSUE SHEET (HEAVY WEIGHT)	VALUE	UNITS
Forming speed/reel speed	1852/1519	ft/min.
Furnish	50% SWK (Naheola Pine)	---
	50% HWK (Naheola Gum)	
Refining (softwood only)	25	hp
Stratification	Homogeneous	---
MD/CD tensile ratio	2.0 - 2.5	---
Basis weight	16.6	lb./ream*
Dry stock flow	16	lb./min
Yankee steam/Hood temp.	100/700 (start pts.)	psig/deg. F
Infrared heater	ON	---
Moisture	4	%
Calender load	"low load"	---
Reel crepe	18	%
Crepe blade bevel	15	deg.

*Ream = 3000 Sq. ft.
 1 lb/ream = 1.63g/m²
 1 lb/min = 7.56 g/sec
 1 psig = 6.89 kPa
 700°F = 371°C

Example 3

[0061] A furnish of 50% Southern hardwood kraft and 50 % Southern softwood kraft was prepared. The papermaking machine was an inclined wire former with a Yankee dryer speed of 3450 feet per minute. The operating data for the papermaking process are set forth in Table 3. A low basis weight base sheet was prepared.

Table 3

TWO PLY TISSUE SHEET (LIGHT WEIGHT)	VALUE	UNITS
Forming speed	(3450) 17.5	(ft/min.) m/sec
Reel crepe	18	%
Yankee steam pressure	(75) 517	(psi) kPa
Wet end hood temperature	(550) 288	(deg. F) °C
Jet/wire ratio	0.94	---
Headbox slice	(0.500) 12.7	(in) mm
Refiner flow	(48) 3.0	(gal/min.) l/sec
Total headbox flow	(1980) 125	(gal/min.) l/sec
Refining (softwood only)	42	hp
Basis weight	(9.6) 15.6	(lb./ream*) g/m ²
Moisture	4	%
Crepe blade bevel	15	deg.

*Ream = 3000 Sq. feet

Example 4

[0062] Table 4 provides the chemical code designation and description of the adhesives, crosslinking agents, softeners, and release agents employed in Examples 1, 5, 6, 7 and 8.

Table 4

Descriptions of Chemical Compounds Used In Examples 5-8 and Figures 3 - 5	
CHEMICAL DESIGNATION	COMMENTS
H8290 (PAE)	Houghton Rezoso [®] 8290 adhesive (polyaminoamide-epichlorohydrin)
A1	Polyvinyl alcohol - 6 mol % vinyl amine copolymer
GLYOXAL	Crosslinking agent for A1, supplied by Hoechst Celanese as 40 % solution
AZC	Ammonium zirconium carbonate (crosslinking agent for A1), supplied by Magnesium Elektron, Inc. as 20 % solution (BACOTE [®] 20)
202-JR	Quaker Quasoft [®] 202-JR softener (fatty diamide quat based on diethylene triamine and C14-C18 unsaturated fatty acids)
H565	Houghton 565 release (mineral oil based)
AIRVOL - 107	Polyvinyl Alcohol (Mol. Wt. = 40,000 g/mol, Hydrolysis = 98 mol%), supplied by Air Products and Chemicals, Inc.
AIRVOL - 540	Polyvinyl Alcohol (Mol. Wt. = 155,000 g/mol, Hydrolysis = 88 mol%), supplied by Air Products and Chemicals, Inc.
AIRVOL - 350	Polyvinyl Alcohol (Mol. Wt. = 155,000 g/mol, Hydrolysis = 98 mol%), supplied by Air Products and Chemicals, Inc.
AIRVOL - 205	Polyvinyl Alcohol (Mol. Wt. = 40,000 g/mol, Hydrolysis = 88 mol%), supplied by Air Products and Chemicals, Inc.

Example 5

[0063] This example gives the adhesive formulations for papermaking process described in Examples 6, 7 and 8. In Tables 5, 6 and 7 data has been set forth for each of the 17 cells. Table 5 summarizes these examples and lists the cell number, base polymer, glyoxal, ammonium zirconium carbonate, softener, release agent and states whether the furnish was refined or unrefined and gives the basis weight of the paper sheet. The sheet tension values and sidedness parameters are not given in this table but are set forth in Tables 6, 7 and 8 where applicable.

Table 5

	BASE POLY-MER (0.2 #/T)	GLYOXAL (#/T)	AZC (#/T)	202-JR (#/T)	H565 (#/T)	REFINING (1) (HP)	BASIS WEIGHT (#/REAM)
1	A1	0.2	---	1.0	0.25	NONE	16.6
2	A1	0.2	---	1.0	0.25	25	16.6
3	H8290 (PAE)	---	---	1.0	0.25	25	16.6
4	A1	---	0.02	1.0	0.25	NONE	16.6
5	A1	---	0.10	1.0	0.25	NONE	16.6
6	A1	---	0.02	1.0	0.25	25	16.6
7	A1	---	0.10	1.0	0.25	25	16.6
8	A1	---	---	1.0	0.25	NONE	16.6
9	H8290 (PAE)	---	---	1.0	0.25	NONE	16.6
10	A1	---	---	1.0	0.25	25	16.6
11	A1	0.4	---	1.0	0.25	NONE	16.6
12	A1	0.2	---	1.0	0.25	NONE	16.6
13	A1	0.4	---	1.0	0.25	25	16.6
14	H8290 (PAE)	---	---	---	2.5	42	9.6
15	A1	---	0.02	---	2.5	42	9.6
16	A1	---	0.04	---	2.5	42	9.6
17	A1	0.4	---	---	2.5	42	9.6

(1) Refining softwood only

(#/T) = pounds per ton of furnish

1 pound per ton = 0.5 g/kg

1 pound per ream = 1.63 g/m²

Example 6

[0064] This example illustrates that when the adhesive consisting of PVOH-VAM copolymer crosslinked with AZC is used, sheet tension values are obtained which are equivalent or better than the values obtained for the commercial PAE control product. The base sheet for the two ply tissue was prepared according to the process of Example 3. The description of the additives, crosslinking agents, and softeners are set forth in Table 5. Sheet tension and corresponding base sheet properties achieved with the PVOH-VAM copolymer crosslinked with glyoxal or ammonium zirconium carbonate package are at least as good as or better than the undesirable chlorine containing Houghton 8290 (PAE) adhesive. The data is set forth in Table 6. The ammonium zirconium carbonate package is superior to the PAE resin package and also to the glyoxal crosslinking package as evidenced by lower STFI length and friction parameters. It should be noted that glyoxal is added to the PVOH-VAM copolymer just prior to spraying on the Yankee dryer while the ammonium zirconium carbonate is sprayed separately but simultaneously with the PVOH-VAM copolymer.

Table 6

Low Basis Weight Basesheet Data For Two Ply Tissue (Refining level = 42 Hp)							
CELL	FORMULATION	SHEET TENSION (G/24 IN)	BASIS WEIGHT (#/ream)	GMT (G/3 IN)	STFI* LENGTH (μ M)	STIFFNESS (G/%STR.-IN)	FRICTION
14 (control)	0.2 #/T H8290 PAE 2.5 #/T H565	1038 \pm 8	9.6	427	131	35.7	0.15
15	0.2 #/T A1 0.02 #/T AZC 2.5 #/T H565	1039 \pm 18	9.9	446	121	34.0	0.14
16	0.2 #/T A1 0.04 #/T AZC 2.5 #/T H565	1057 \pm 13	9.5	414	125	36.3	0.14
17	0.2 #/T A1 0.4 #/T GLYOXAL 2.5 #/T H565	1085 \pm 5	9.3	384	129	30.1	0.15
#/T H8290 PAE = pounds of adhesive per ton of furnish #/T H565 = pounds of release agent per ton of furnish #/T A1 = pounds of adhesive per ton of furnish #/T AZC = pounds of crosslinking agent per ton of furnish #/T GLYOXAL = pounds of crosslinking agent per ton of furnish							

* STFI values determined from publication at *Tissue Making Conference*, October 5-6, 1989 in Karlstad, Sweden, *Characterization of Crepe Structure by Image Analysis*, Magnus Falk, STFI Sweden, pp. 39-50.

1 g/24 in = 1.64 g/m

1 g/3 in = 13 g/m

1 lb/ream = 1.63 g/m²

Example 7

[0065] This example illustrates that using the novel adhesive formulations with softeners facilitated the production of low sidedness one ply tissue. The base sheet for the one ply tissue was prepared according to the papermaking process of Example 2. The data for this Example are set forth in Table 7. The data in Table 7 clearly demonstrate the adhesive capacity of ammonium zirconium carbonate and glyoxal crosslinking agents. In this example softeners are used to reduce the sidedness of the one ply tissue. The data demonstrate that our novel adhesive formulations are compatible with softeners.

Table 7

High Basis Weight Basesheet Data (No Refining) For One Ply Tissue								
CELL	FORMULATION	SHEET TENSION (G/24 IN)	BW (#/ream)	GMT (G/3 IN)	STFI* LENGTH (μ M)	STIFFNESS (G/% STR.-IN)	FRIC-TION	S ⁽¹⁾
9 (control)	0.2 #/T H8290 PAE 1.0 #/T 202-JR 0.25 #/T H565	600 \pm 17	16.4	598	167	18.5	0.22	0.31
8	0.2 #/T A1 1.0 #/T 202-JR 0.25 #/T H565	308 \pm 8	16.2	747	171	23.1	0.23	0.32
4	0.2 #/T A1 0.02 #/T AZC 1.0 #/T 202-JR 0.25 #/T H565	375 \pm 47	17.3	752	172	22.9	0.23	0.23
5	0.2 #/T A1 0.10 #/T AZC 1.0 #/T 202-JR 0.25 #/T H565	433 \pm 21	16.6	667	166	22.7	0.19	0.21
12	0.2 #/T A1 0.2 #/T GLYOXAL 1.0 #/T 202-JR 0.25 #/T H565	267 \pm 32	16.1	695	180	23.7	0.23	0.31
11	0.2 #/T A1 0.4 #/T GLYOXAL 1.0 #/T 202-JR 0.25 #/T H565	372 \pm 36	17.1	752	179	22.0	0.22	0.30

(1)S = SIDEDNESS PARAMETER - (A/Y)GMMMD WHERE A AND Y ARE RESPECTIVELY AIR SIDE AND YANKEE SIDE FRICTION. LOWER S VALUES ARE DESIRABLE.

#/T H8290 PAE = pounds of adhesive per ton of furnish

#/T H565 = pounds of release agent per ton of furnish

#/T A1 = pounds of adhesive per ton of furnish

#/T AZC = pounds of crosslinking agent per ton of furnish

#/T GLYOXAL = pounds of crosslinking agent per ton of furnish

#/T 202-JR = pounds of softener per ton of furnish

* STFI values determined from publication at *Tissue Making Conference*, October 5-6, 1989 in Karlstad, Sweden, *Characterisation of Crepe Structure by Image Analysis*, Magnus Falk, STFI, Sweden, pp. 39-50.

For conversions to S1 units, see Table 6

Example 8

[0066] This example illustrates that using our novel adhesive formulations, high sheet tension is maintained, while giving the one ply tissue a low sidedness parameter relative to PAE control. The base sheet for one ply was prepared according to the papermaking process of Example 2. The difference between Examples 7 and 8 is that in this example

EP 0 743 172 B1

the furnish was refined. The data in Table 8 demonstrate adhesive capacity of the base polymer when coming in contact on the Yankee surface with the dialdehyde or zirconium crosslinking agent in the presence of a softener resulting in lower stiffness values relative to PAE control. Using the refined furnish higher sheet tension values are obtained in the presence of a softener while still having a good sidedness parameter.

Table 8

High Basis Weight Basesheet Data (Refining Level = 25 Hp) For One Ply Tissue								
CELL	FORMULATION	SHEET TENSION (G/24 IN)	BW (#/RM)	GMT (G/3 IN)	STFI* LENGTH (μM)	STIFFNESS (G/%STR.-IN)	FRIC-TION	S ⁽¹⁾
3 (control)	0.2 #/T H8290 PAE 1.0 #/T 202-JR 0.25 #/T H565	786 ± 64	17.1	1054	150	37.6	0.21	0.34
10	0.2 #/T A1 1.0 #/T 202-JR 0.25 #/T H565	866 ± 48	17.1	1041	158	31.9	0.24	0.32
6	0.2 #/T A1 0.02 #/T AZC 1.0 #/T 202-JR 0.25 #/T H565	880 ± 29	16.6	1046	174	30.6	0.23	0.34
7	0.2 #/T A1 0.10 #/T AZC 1.0 #/T 202-JR 0.25 #/T H565	999 ± 50	16.6	1016	152	31.1	0.21	0.25
2	0.2 #/T A1 0.2 #/T GLYOXAL 1.0 #/T 202-JR 0.25 #/T H565	755 ± 80	17.7	1193	170	32.9	0.23	0.32
13	0.2 #/T A1 0.4 #/T GLYOXAL 1.0 #/T 202-JR 0.25 #/T H565	841 ± 38	17.2	1075	163	34.1	0.24	0.35

(1) S = SIDEDNESS PARAMETER = (A/Y)GMMMD WHERE A AND Y ARE RESPECTIVELY, AIR SIDE AND YANKEE SIDE FRICTION. LOWER S VALUES ARE DESIRABLE.

#/T H8290 PAE = pounds of adhesive per ton of furnish #/T H565 = pounds of release agent per ton of furnish

#/T A1 = pounds of adhesive per ton of furnish

#/T AZC = pounds of crosslinking agent per ton of furnish

#/T GLYOXAL = pounds of crosslinking agent per ton of furnish

#/T 202-JR = pounds of softener per ton of furnish

* STFI values determined from publication at *Tissue Making Conference*, October 5-6, 1989 in Karlstad, Sweden, *Characterisation of Crepe Structure by Image Analysis*, Magnus Falk, STFI, Sweden, pp. 39-50.

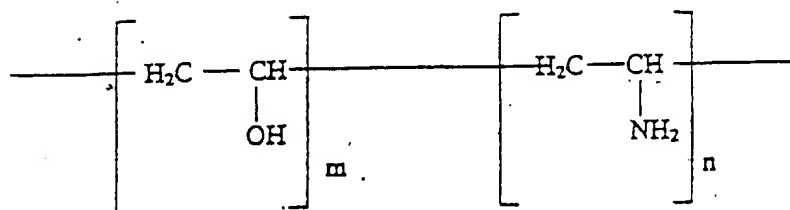
For conversions to S1 units, see Table 6

Claims

1. A creping adhesive composition comprising an organic polymer having in the polymer backbone amine groups

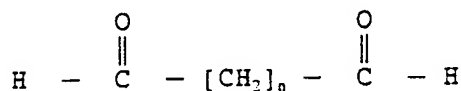
selected from primary and secondary amine groups and mixtures thereof and a crosslinking agent for crosslinking the polymer to itself and to the fibrous web, said agent being selected from zirconium compounds wherein the zirconium has a valency of plus four.

2. An adhesive composition as claimed in claim 1 characterised in that the organic polymer is selected from chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.
3. An adhesive composition as claimed in claim 1 or claim 2 characterised in that the crosslinking agent is selected from ammonium zirconium carbonate, zirconium acetylacetonate, zirconium acetate, zirconium carbonate, zirconium sulfate, zirconium phosphate, potassium zirconium carbonate, zirconium sodium phosphate and sodium zirconium tartrate.
4. An adhesive composition as claimed in any one of the preceding claims characterised in that the organic polymer is selected from polyvinyl alcohol-vinyl amine copolymers of the following structure:



wherein m and n have values of 1 to 99 and 99 to 1 respectively.

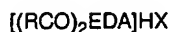
5. A creped fibrous web made using, as the creping adhesive, an adhesive composition as claimed in any one of claims 1 to 4.
6. A creped fibrous web as claimed in claim 5 characterised in that it includes a nitrogenous softener/debonder.
7. A creped fibrous web made using, as the creping adhesive, a composition comprising an organic polymer having in the polymer backbone amine groups selected from primary and secondary amine groups and mixtures thereof and a crosslinking agent for crosslinking the polymer to itself and to the fibrous web, said agent being selected from dialdehydes said web further including a nitrogenous softener/debonder.
8. A creped fibrous web as claimed in claim 7 characterised in that the dialdehyde has the following structure:



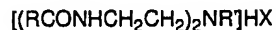
wherein n is an integer having a value of 0 to 3.

9. A creped fibrous web as claimed in claim 7 characterised in that dialdehyde is glyoxal.
10. A creped fibrous web as claimed in any one of claims 6 to 9 characterised in that the softener/debonder is employed in an amount of from 0.1 to 10lbs per ton of the cellulosic papermaking fibers in the aqueous furnish.
11. A creped fibrous web as claimed in any one of claims 6 to 10 characterised in that the nitrogenous softener/debonder is selected from imidazolines, amido amine salts, linear amido amines, tetravalent ammonium salts, and mixtures thereof.
12. A creped fibrous web as claimed in any one of claims 6 to 11 characterised in that the softener/debonder has the

following structure:



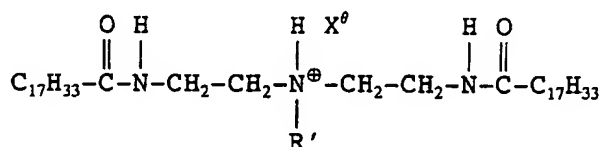
wherein EDA is a diethylenetriamine residue, R is the residue of a fatty acid having from 12 to 22 carbon atoms, and X is an anion, or



wherein R is the residue of a fatty acid having from 12 to 22 carbon atoms, R' is a lower alkyl group, and X is an anion.

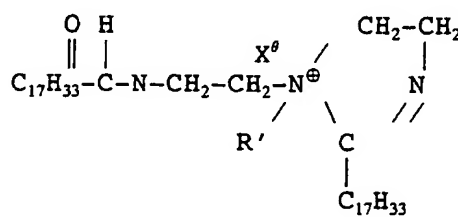
13. A creped fibrous web as claimed in any one of claims 6 to 12 characterised in that the softener/debonder is a mixture of linear amido amines and imidazolines of the following structure:

(i)



and

(ii)



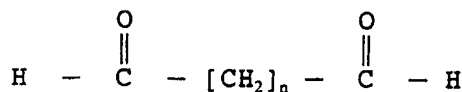
wherein X is an anion.

14. A creped fibrous web as claimed in any one of claims 5 to 13 characterised in that from 0.05 to 0.4 kg (0.1 to 0.8 pounds) of the adhesive formulation are employed for each ton of cellulosic papermaking fibers in the aqueous furnish.
15. A creped fibrous web as claimed in any one of claims 5 to 14 characterised in that the organic polymer is selected from chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.
16. A creped fibrous web as claimed in any one of claims 5 to 15 in the form of a creped towel or a creped tissue.
17. A method of creping a fibrous web which includes adhering it to a dryer surface with a creping adhesive composition and thereafter creping it from the surface characterised in that said adhesive composition is selected from adhesive compositions as claimed in any one of claims 1 to 4.
18. A method as claimed in claim 17 characterised in that the crosslinking agent and organic polymer are applied separately to the dryer surface whereby crosslinking takes place on the dryer surface.
19. A method as claimed in claim 17 characterised in that the crosslinking agent and organic polymer are mixed together just prior to contact with the dryer surface whereby crosslinking substantially takes place on the dryer surface.
20. A method of creping a fibrous web which includes adhering it to a dryer surface with a creping adhesive composition and thereafter creping it from the surface characterised in that the creping adhesive composition comprises an organic polymer having in the polymer backbone amine groups selected from primary and secondary amine

groups and mixtures thereof and a crosslinking agent for crosslinking the polymer to itself and to the fibrous web said agent being selected from dialdehydes, and the crosslinking agent and organic polymer are applied separately to the dryer surface whereby crosslinking takes place on the dryer surface.

21. A method of creping a fibrous web which includes adhering it to a dryer surface with a creping adhesive composition and thereafter creping it from the surface characterised in that the creping adhesive composition comprises an organic polymer having in the polymer backbone amine groups selected from primary and secondary amine groups and mixtures thereof and a crosslinking agent for crosslinking the polymer to itself and to the fibrous web said agent being selected from dialdehydes, and the crosslinking agent and organic polymer are mixed together just prior to contact with the dryer surface whereby crosslinking substantially takes place on the dryer surface.

22. A method as claimed in claim 20 or claim 21 characterised in that the dialdehyde has the following structure:



wherein n is an integer having a value of 0 to 3.

23. A method as claimed in claim 20 or claim 21 characterized in that the dialdehyde is glyoxal.

24. A method as claimed in any one of claims 17 to 23 characterized in that 0.05 to 0.4 kg (0.1 to 0.8 pounds) of the adhesive are added for each ton of cellulosic papermaking fibers in the aqueous furnish.

25. A method as claimed in any one of claims 17 to 24 characterised in that a nitrogenous softener/debonder is included in the fibrous web.

26. A method as claimed in claim 25 characterized in that 0.1 to 10 pounds of cationic softener/debonder are added for each ton of the cellulosic papermaking fibers in the aqueous furnish.

27. A method as claimed in claim 25 or claim 26 characterized in that the nitrogenous softener/debonder is as specified in any one of claims 11 to 13.

28. A method as claimed in any one of claims 19 to 27 characterised in that the organic polymer is selected from chitosan, polyvinylamine, polyvinyl alcohol-vinyl amine and polyaminoamide.

29. A method as claimed in any one of claims 17 to 28 characterized in that the fibrous web is a towel or tissue.

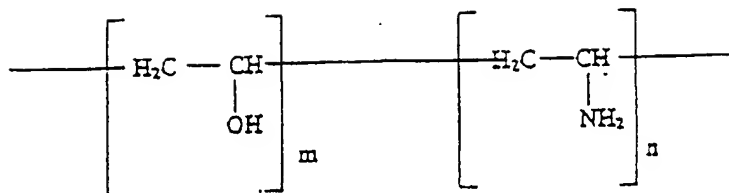
Patentansprüche

1. Klebstoffzusammensetzung zum Kreppén, umfassend ein organisches Polymer, das in seiner Hauptkette aus primären und sekundären Amingruppen sowie deren Mischungen ausgewählte Amingruppen aufweist, und ein Vernetzungsmittel zum Vernetzen des Polymeren mit sich selbst und dem Fasergewebe, wobei das Mittel aus Zirkoniumverbindungen ausgewählt ist, in denen das Zirkonium eine Valenz von +4 hat.

2. Klebstoffzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das organische Polymer aus Chitosan, Polyvinylamin, Polyvinylalkohol-Vinylamin und Polyaminoamid ausgewählt wird.

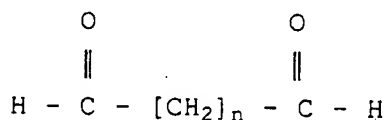
3. Klebstoffzusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Vernetzungsmittel aus Ammoniumzirkoniumcarbonat, Zirkoniumacetylacetonat, Zirkoniumacetat, Zirkoniumcarbonat, Zirkoniumsulfat, Zirkoniumphosphat, Kaliumzirkoniumcarbonat, Zirkoniumnatriumphosphat und Natriumzirkoniumtartrat ausgewählt wird.

4. Klebstoffzusammensetzung nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das organische Polymer aus Polyvinylalkohol-Vinylamin-Copolymeren der folgenden Struktur ausgewählt wird

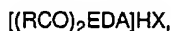


in der m und n Werte von 1 bis 99 bzw. 99 bis 1 haben.

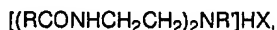
5. Gekrepptes Fasergewebe, das unter Verwendung einer Klebstoffzusammensetzung nach einem der Ansprüche 1 bis 4 als Klebstoff zum Kreppen hergestellt wird.
6. Gekrepptes Fasergewebe nach Anspruch 5, dadurch gekennzeichnet, daß es einen stickstoffhaltigen Weichmacher/Bindungslöser umfaßt.
7. Gekrepptes Fasergewebe, hergestellt unter Verwendung einer Klebstoffzusammensetzung zum Kreppen, die ein organisches Polymer, das in seiner Hauptkette aus primären und sekundären Amingruppen sowie deren Mischungen ausgewählte Amingruppen aufweist, und ein aus Dialdehyden ausgewähltes Vernetzungsmittel zum Vernetzen des Polymeren mit sich selbst und dem Fasergewebe umfaßt, wobei das Gewebe außerdem einen stickstoffhaltigen Weichmacher/Bindungslöser umfaßt.
8. Gekrepptes Fasergewebe nach Anspruch 7, dadurch gekennzeichnet, daß das Dialdehyd die folgende Struktur



- aufweist, in der n eine ganze Zahl mit einem Wert von 0 bis 3 ist.
9. Gekrepptes Fasergewebe nach Anspruch 7, dadurch gekennzeichnet, daß das Dialdehyd Glyoxal ist.
 10. Gekrepptes Fasergewebe nach einem der Ansprüche 6 bis 9, dadurch gekennzeichnet, daß der Weichmacher/Bindungslöser in einer Menge von 0,1 bis 10 lbs pro Tonne Cellulosefasern zum Papiermachen in der wäßrigen Beschickung verwendet wird.
 11. Gekrepptes Fasergewebe nach einem der Ansprüche 6 bis 10, dadurch gekennzeichnet, daß der stickstoffhaltige Weichmacher/Bindungslöser aus Imidazolin, Amidoaminsalzen, linearen Amidoaminen, vierwertigen Ammoniumsalzen und deren Mischungen ausgewählt wird.
 12. Gekrepptes Fasergewebe nach einem der Ansprüche 6 bis 11, dadurch gekennzeichnet, daß der Weichmacher/Bindungslöser die Struktur

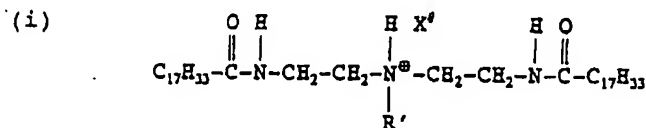


in der EDA ein Diethylentriaminrest ist, R den Rest einer Fettsäure mit 12 bis 22 Kohlenstoffatomen darstellt und X ein Anion ist, oder

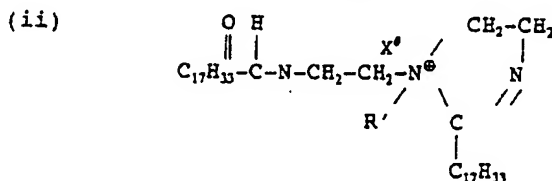


in der R den Rest einer Fettsäure mit 12 bis 22 Kohlenstoffatomen und R' eine niedere Alkylgruppe darstellt und X ein Anion ist, hat.

13. Gekrepptes Fasergewebe nach einem der Ansprüche 6 bis 12, dadurch gekennzeichnet, daß der Weichmacher/Bindungslöser ein Gemisch aus linearen Amidoaminen und Imidazolen der folgenden Struktur



und

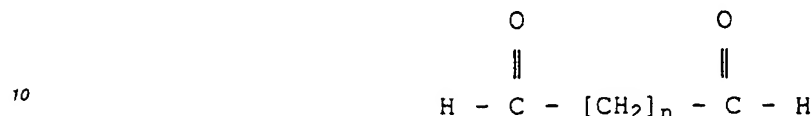


ist, in der X ein Anion ist.

14. Gekrepptes Fasergewebe nach einem der Ansprüche 5 bis 13, dadurch gekennzeichnet, daß 0,05 bis 0,4 kg (0,1 bis 0,8 pounds) der Klebstoffformulierung pro Tonne Cellulosefasern zum Papiermachen in der wäßrigen Beschik-
kung verwendet werden.
15. Gekrepptes Fasergewebe nach einem der Ansprüche 5 bis 14, dadurch gekennzeichnet, daß das organische Polymer aus Chitosan, Polyvinylamin, Polyvinylalkohol-Vinylamin und Polyaminoamid ausgewählt wird.
16. Gekrepptes Fasergewebe nach einem der Ansprüche 5 bis 15 in Form eines gekreppten Handtuchs oder Tissue-
tuchs.
17. Verfahren zum Kreppen eines Fasergewebes, bei dem das Gewebe mit einer Klebstoffzusammensetzung zum
Kreppen haftend auf die Oberfläche eines Trockners aufgebracht und dann von der Oberfläche gekreppt wird,
dadurch gekennzeichnet, daß die Klebstoffzusammensetzung aus Klebstoffzusammensetzungen nach einem der
Ansprüche 1 bis 4 ausgewählt wird.
18. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß das Vernetzungsmittel und das organische Polymer
getrennt auf die Trockneroberfläche aufgebracht werden, wodurch die Vernetzung auf der Trockneroberfläche
erfolgt.
19. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß das Vernetzungsmittel und das organische Polymer
unmittelbar vor dem Kontakt mit der Trockneroberfläche miteinander vermischt werden, wodurch die Vernetzung im
wesentlichen auf der Trockneroberfläche erfolgt.
20. Verfahren zum Kreppen eines Fasergewebes, bei dem man dieses mit einer Klebstoffzusammensetzung zum
Kreppen haftend auf eine Trockneroberfläche aufbringt und anschließend von der Oberfläche kreppt, dadurch
gekennzeichnet, daß die Klebstoffzusammensetzung zum Kreppen ein organisches Polymer, das in der Polymer-
hauptkette aus primären und sekundären Amingruppen und deren Mischungen ausgewählte Amingruppen auf-
weist, sowie ein aus Dialdehyden ausgewähltes Vernetzungsmittel zum Vernetzen des Polymeren mit sich selbst
und dem Fasergewebe umfaßt, und das Vernetzungsmittel und das organische Polymer getrennt auf die Trockner-
oberfläche aufbringt, wodurch die Vernetzung auf der Trockneroberfläche erfolgt.
21. Verfahren zum Kreppen eines Fasergewebes, bei dem man dieses mit einer Klebstoffzusammensetzung zum
Kreppen haftend auf eine Trockneroberfläche aufbringt und anschließend von der Oberfläche kreppt, dadurch
gekennzeichnet, daß die Klebstoffzusammensetzung zum Kreppen ein organisches Polymer, das in der Polymer-
hauptkette aus primären und sekundären Amingruppen und deren Mischungen ausgewählte Amingruppen auf-
weist, sowie ein aus Dialdehyden ausgewähltes Vernetzungsmittel zum Vernetzen des Polymeren mit sich selbst

und dem Fasergewebe umfaßt, und das Vernetzungsmittel und das organische Polymer unmittelbar vor dem Kontakt mit der Trockneroberfläche vermischt, wodurch die Vernetzung im wesentlichen auf der Trockneroberfläche erfolgt.

- 5 22. Verfahren nach Anspruch 20 oder 21, dadurch gekennzeichnet, daß das Dialdehyd die folgende Struktur



aufweist, in der n eine ganze Zahl mit einem Wert von 0 bis 3 ist.

15

23. Verfahren nach Anspruch 20 oder 21 dadurch gekennzeichnet, daß das Dialdehyd Glyoxal ist.

24. Verfahren nach einem der Ansprüche 17 bis 23, dadurch gekennzeichnet, daß 0,05 bis 0,4 kg (0,1 bis 0,8 pounds) Klebstoff für jede Tonne Cellulosefasern zum Papiermachen in der wäßrigen Beschickung zugesetzt werden.

20

25. Verfahren nach einem der Ansprüche 17 bis 24, dadurch gekennzeichnet, daß ein stickstoffhaltiger Weichmacher/Bindungslöser im Fasergewebe enthalten ist.

26. Verfahren nach Anspruch 25, dadurch gekennzeichnet, daß der Weichmacher/Bindungslöser in einer Menge von 0,1 bis 10 lbs pro Tonne Cellulosefasern zum Papiermachen in der wäßrigen Beschickung zugesetzt wird.

25

27. Verfahren nach Anspruch 25 oder 26, dadurch gekennzeichnet, daß der stickstoffhaltige Weichmacher/Bindungslöser der Spezifikation in einem der Ansprüche 11 bis 13 entspricht.

- 30 28. Verfahren nach einem der Ansprüche 19 bis 27, dadurch gekennzeichnet, daß das organische Polymer aus Chitosan, Polyvinylamin, Polyvinylalkohol-Vinylamin und Polyaminoamid ausgewählt wird.

29. Verfahren nach einem der Ansprüche 17 bis 28, dadurch gekennzeichnet, daß das Fasergewebe ein Handtuch oder Tissuetuch ist.

35

Revendications

1. Composition adhésive de crépage comprenant un polymère organique dans les groupes amines à squelette polymère choisi à partir de groupes amines primaire et secondaire et leurs mélanges et un agent de réticulation pour réticuler le polymère en lui même et en bande fibreuse, l'agent étant sélectionné à partir de composés de zirconium dans lesquels le zirconium a une valence de plus quatre.

40

2. Composition adhésive selon la revendication 1, caractérisée en ce que le polymère organique est choisi à partir de polyvinyle amine, polyvinyle alcool vinyle amine et polyaminoamide.

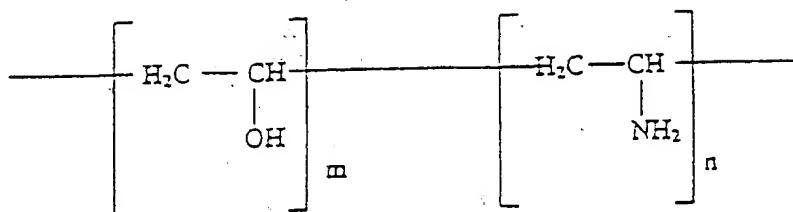
45

3. Composition adhésive selon la revendication 1 ou 2, caractérisée en ce que l'agent réticulation est choisi à partir de carbonate de zirconium d'ammonium, d'acétylacétonate de zirconium, d'acétate de zirconium, de carbonate de zirconium, de sulfate de zirconium, de phosphate de zirconium, de carbonate de zirconium potassium, de phosphate de sodium de zirconium et de tartrate de zirconium sodium.

50

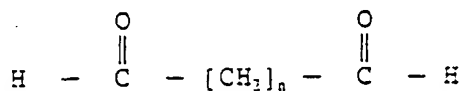
4. Composition adhésive selon l'une quelconque des revendications précédentes, caractérisée en ce que le polymère organique est choisi à partir de copolymère de polyvinyle alcool-vinyle amine de la structure suivante :

55



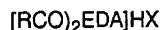
dans laquelle m et n ont les valeurs de 1 à 99 et 99 à 1 respectivement.

5. Bande continue fibreuse crêpée, réalisée en utilisant, comme substance adhésive de crêpage, une composition adhésive selon l'une quelconque des revendications 1 à 4.
6. Bande fibreuse crêpée selon la revendication 5, caractérisée en ce qu'elle comprend un agent plastifiant azoté/délicant.
7. Bande fibreuse crêpée réalisée en utilisant comme adhésif de crêpage, une composition comprenant un polymère organique avec dans le squelette polymère des groupes amines choisis à partir de groupes amines primaires et secondaires et leurs mélanges et un agent réticulant pour réticuler le polymère en lui même et en la bande fibreuse, l'agent étant choisi à partir de dialdéhydes, la bande comprenant de plus un agent plastifiant azoté/délicant.
8. Bande fibreuse crêpée selon la revendication 7, caractérisée en ce que le dialdéhyde est la structure suivante :

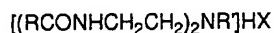


dans laquelle n est un nombre entier ayant une valeur de 0 à 3.

9. Bande fibreuse crêpée selon la revendication 7, caractérisée en ce que le dialdéhyde est du glyoxal.
10. Bande fibreuse crêpée selon l'une quelconque de revendications 6 à 9, caractérisée en ce que l'agent plastifiant/délicant est employé dans une quantité de 0,1 à 10 livres par tonne de la fibre de fabrication de papier cellulosique dans la matière aqueuse.
11. Bande fibreuse crêpée selon l'une quelconque des revendications 6 à 10, caractérisée en ce que l'agent plastifiant azoté/délicant est choisi à partir d'imidazolines, de sels amido amine, d'amido amines linéaires, de sels d'ammonium tétravalent et leurs mélanges.
12. Bande fibreuse crêpée selon l'une quelconque des revendications 6 à 11, caractérisée en ce que l'agent plastifiant/délicant a la structure suivante :



dans laquelle EDA est un résidu de diéthylènetriamine, R est le résidu d'un acide gras ayant de 12 à 22 atomes de carbone et X est un anion, ou

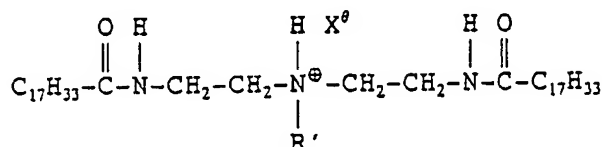


dans laquelle R est le résidu d'un acide gras avec 12 à 22 atomes, R' est un groupe alkyle inférieur et X est un

anion.

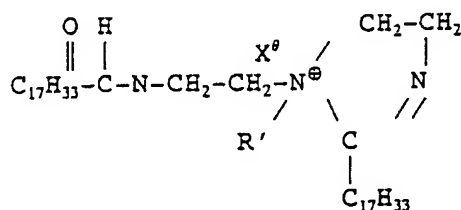
13. Bande fibreuse crêpée selon l'une quelconque des revendications 6 à 12, caractérisée en ce que l'agent plastifiant déliant est un mélange d'amido amines linéaire et d'imidazolines de la structure suivante :

(i)



et

(ii)

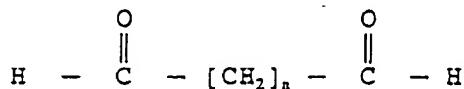


dans laquelle X est un anion.

14. Bande fibreuse crêpée selon l'une quelconque des revendications 5 à 13, caractérisée en ce que de 0,005 à 0,4 Kg (0,1 à 0,8 livres) de la formulation adhésive est employé pour chaque tonne de fibre de fabrication de papier cellulosique dans la matière aqueuse.
15. Bande fibreuse crêpée selon l'une quelconque des revendications 5 à 14, caractérisée en ce que le polymère organique est choisi à partir de chitosan, de polyvinylamine, d'alcool de polyvinyle-vinyle amine et polyaminoamide.
16. Bande fibreuse crêpée selon l'une quelconque des revendications 5 à 15 sous forme d'une serviette crêpée ou d'un tissu crêpé.
17. Procédé de crêpage d'une bande continue fibreuse qui comprend les opérations consistant à faire adhérer sur une surface d'agent sécheur d'une composition adhésive de crêpage et ensuite à crêper à partir de la surface, caractérisé en ce que la composition adhésive est choisie à partir de composition adhésive selon l'une quelconque des revendications 1 à 4.
18. Procédé selon la revendication 18, caractérisé en ce que l'agent de réticulation et le polymère organique sont appliqués séparément sur la surface du sécheur, de sorte que la réticulation s'effectue sur la surface du sécheur.
19. Procédé selon la revendication 17, caractérisé en ce que l'agent de réticulation et le polymère organique sont mélangés ensemble juste avant d'être mis en contact avec la surface du sécheur de sorte que la réticulation s'effectue sensiblement sur la surface du sécheur.
20. Procédé de crêpage d'une bande de continue fibreuse qui comprend les opérations consistant à faire adhérer sur une surface de sécheur, une composition adhésive de crêpage et ensuite à crêper à partir de la surface, caractérisé en ce que la composition adhésive de crêpage comprend un polymère organique ayant dans le squelette polymère des groupes amines choisis à partir de groupes amines primaire et secondaire et leurs mélanges et un agent de réticulation pour réticuler le polymère en lui même et en la bande fibreuse, l'agent étant sélectionné à partir des dialdéhydes, et l'agent de réticulation et le polymère organique sont appliqués séparément sur la surface du sécheur de sorte que la réticulation s'effectue sur la surface du sécheur.
21. Procédé de crêpage d'une bande fibreuse qui comprend les opérations consistant à adhérer sur une surface de sécheur avec une composition adhésive de crêpage et ensuite à crêper à partir de la surface, caractérisé en ce

que la composition adhésive de crêpage comprend un polymère organique ayant dans le squelette polymère des groupes amines choisis à partir de groupes amines primaire et secondaire et leurs mélanges et un agent de réticulation pour réticuler le polymère en lui-même en en la bande fibreuse, l'agent étant choisi à partir de dialdéhydes et l'agent de réticulation et le polymère organique sont mélangés ensemble juste avant de venir en contact avec des surfaces de sécheur de sorte que la réticulation s'effectue sensiblement sur la surface du sécheur.

22. Procédé selon la revendication 20 ou 21, caractérisé en ce que le dialdéhyde a la structure suivante :



dans laquelle n est un nombre entier ayant une valeur de 0 à 3.

23. Procédé selon la revendication 20 ou 21, caractérisé en ce que le dialdéhyde est du glyoxal.

24. Procédé selon l'une quelconque des revendications 17 à 23, caractérisé en ce que l'on ajoute entre 0,05 à 0,4 Kg (0,1 à 0,8 livres) de la matière adhésive pour chaque tonne de fibre de fabrication de papier cellulosique dans le matériau aqueux.

25. Procédé selon l'une quelconque des revendications 17 à 24, caractérisé en ce que l'on incorpore un agent plastifiant azoté/déifiant est incorporé dans la bande continue fibreuse.

26. Procédé selon la revendication 25, caractérisé en ce que l'on ajoute 0,1 à 10 livres d'agent plastifiant cationique/déifiant pour chaque tonne des fibres de fabrication de papier cellulosique dans le matériau aqueux.

27. Procédé selon la revendication 25 ou 26, caractérisé en ce que l'agent plastifiant azoté/déifiant est tel que spécifié dans l'une quelconque des revendications 11 à 13.

28. Procédé selon l'une quelconque des revendications 19 à 27, caractérisé en ce que le polymère organique est choisi à partir de chitosan, polyvinylamine, alcool de polyvinyle-vinylamine et polyaminoamide.

29. Procédé selon l'une quelconque des revendications 17 à 28, caractérisé en ce que la bande continue fibreuse est une serviette ou un tissu.

Fig. 1

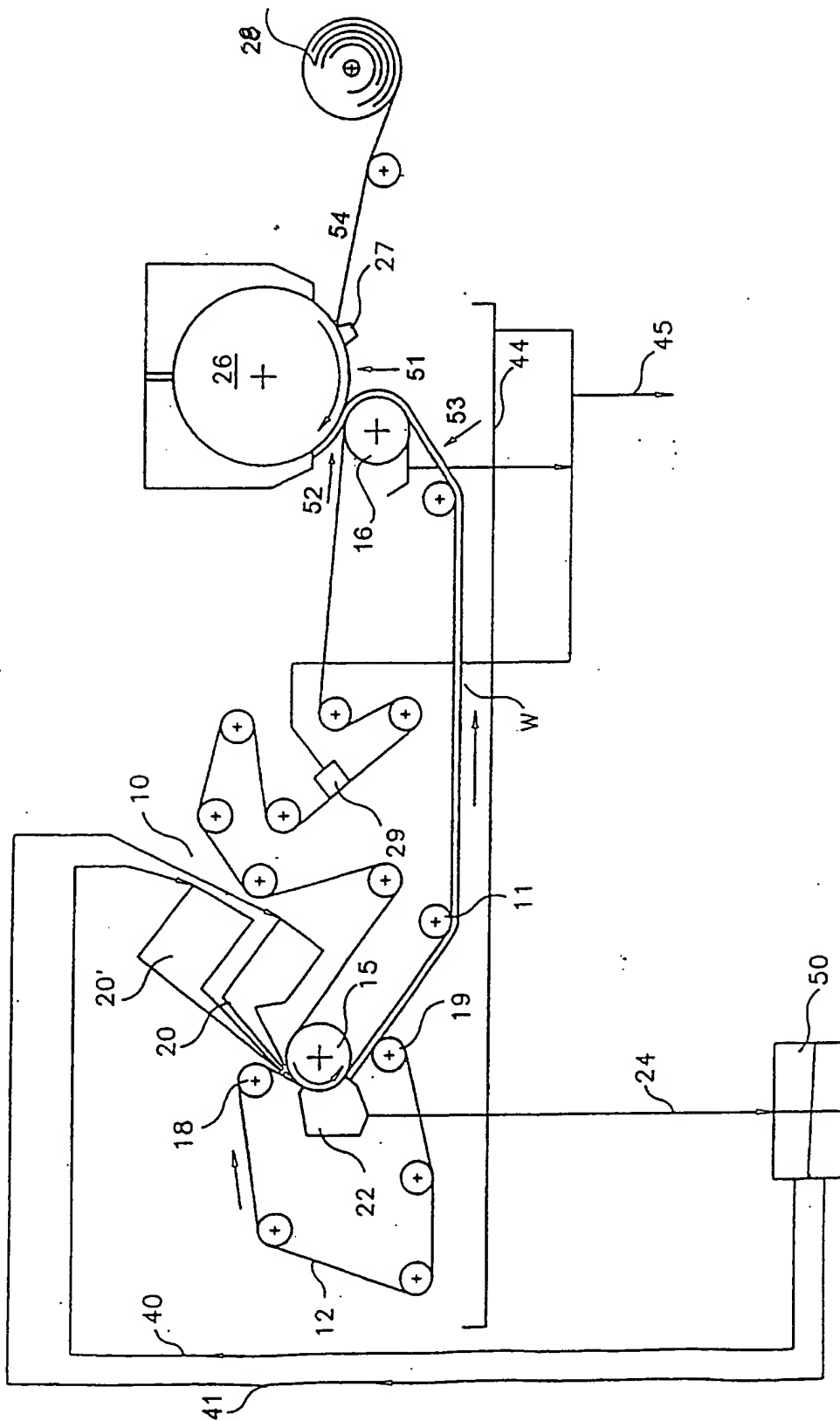


FIGURE 2

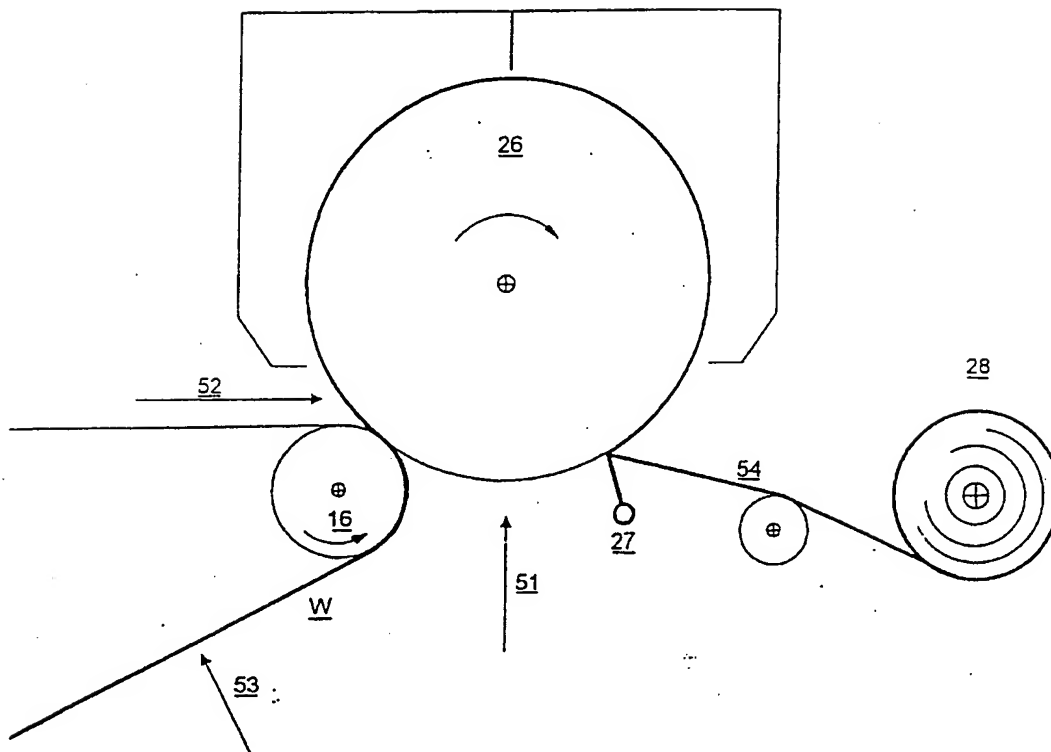


FIGURE 3

PEEL FORCE VERSUS GLYOXAL LEVEL FOR UNFUNCTIONALIZED PVOH

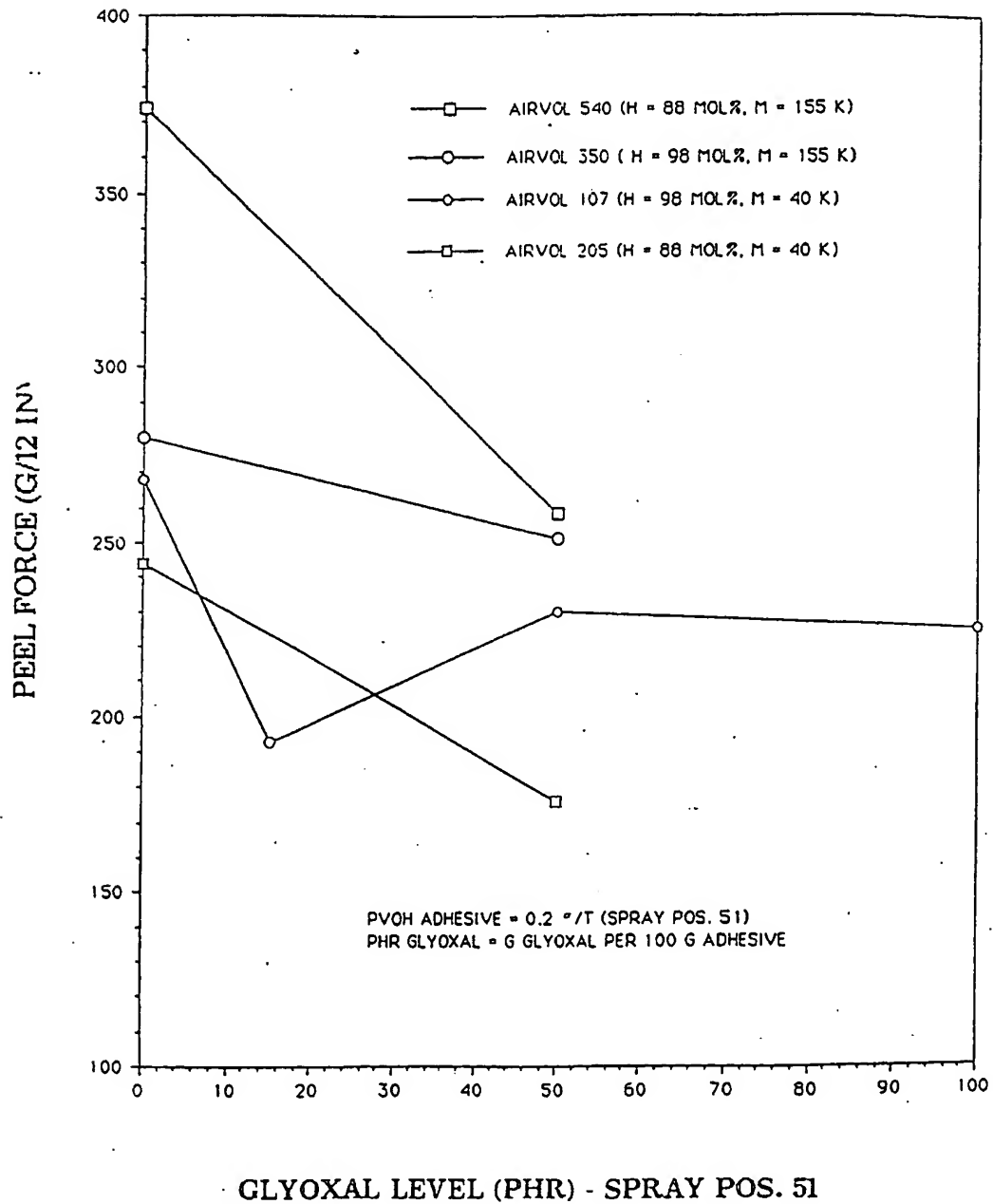


FIGURE 4

PEEL FORCE VERSUS GLYOXAL LEVEL FOR VINYL AMINE
(VA) FUNCTIONALIZED PVOH ADHESIVE

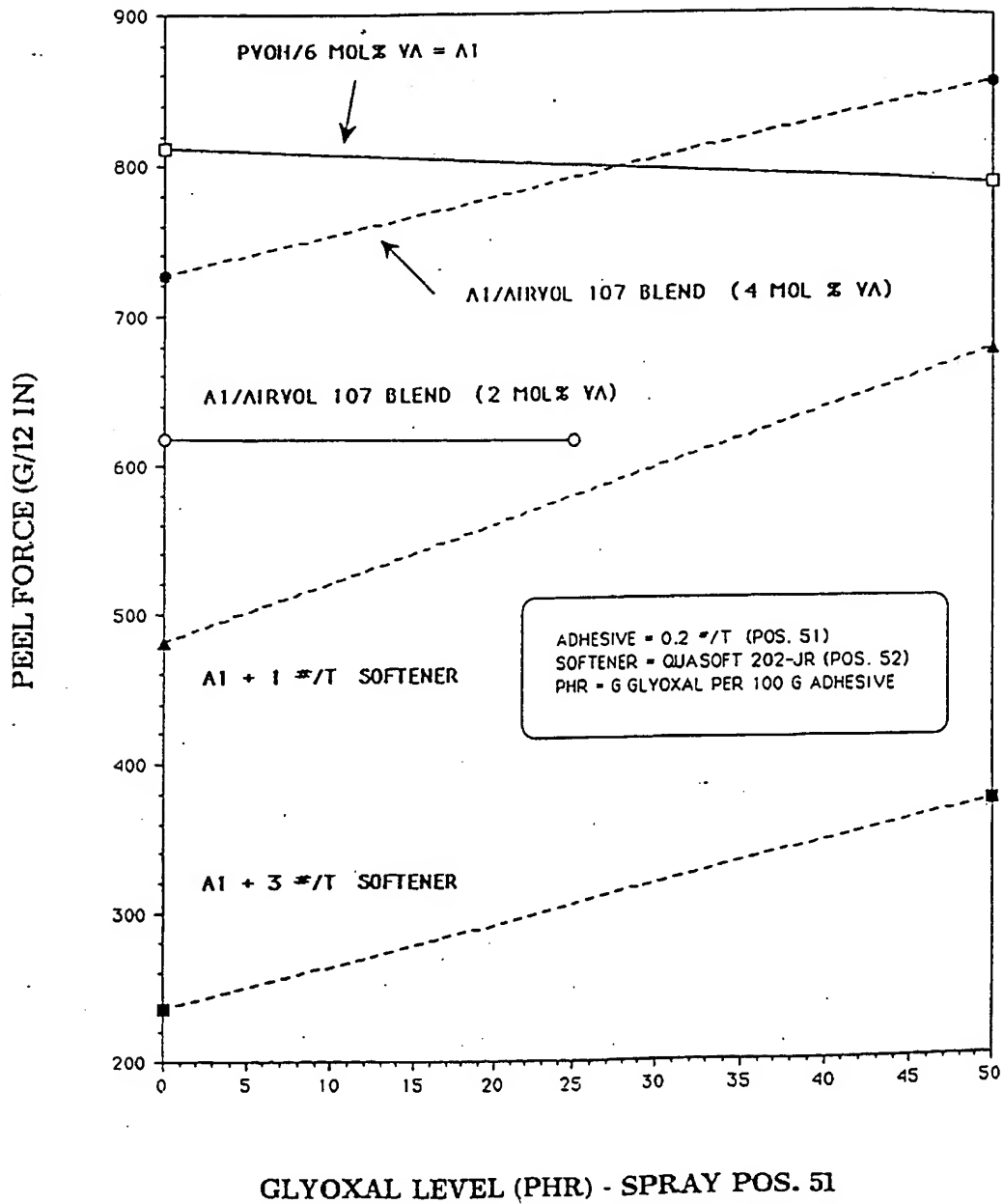


FIGURE 5

GMT VERSUS GLYOXAL LEVEL FOR VINYL
AMINE FUNCTIONALIZED PVOH ADHESIVES

